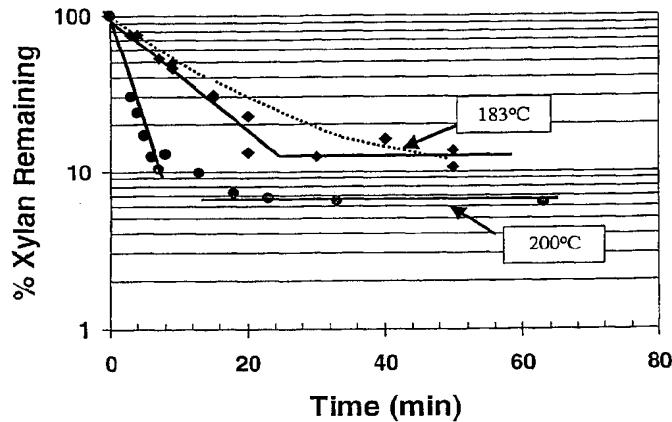




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(71) Applicant (for all designated States except US): MIDWEST RESEARCH INSTITUTE [US/US]; 425 Volker Boulevard, Kansas City, MO 64110 (US).			
(72) Inventor; and			
(75) Inventor/Applicant (for US only): TORGET, Robert, W. [US/US]; 14400 Kuehster Road, Littleton, CO 80127 (US).			
(74) Agent: WHITE, Paul, J.; National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401 (US).			

(54) Title: AQUEOUS FRACTIONATION OF BIOMASS BASED ON NOVEL CARBOHYDRATE HYDROLYSIS KINETICS



## (57) Abstract

A multi-function process for hydrolysis and fractionation of lignocellulosic biomass to separate hemicellulosic sugars from other biomass components comprising extractives and proteins; a portion of a solubilized lignin; cellulose, glucose derived from cellulose; and insoluble lignin from said biomass comprising: a) introducing either solid fresh biomass or partially fractioned lignocellulosic biomass material with entrained acid or water into a reactor and heating to a temperature of up to about 185°C–205°C; b) allowing the reaction to proceed to a point where about 60 % of the hemicellulose has been hydrolyzed in the case of water or complete dissolution in case of; c) adding a dilute acid liquid at a pH below about 5 at a temperature of up to about 205 °C for a period ranging from about 5 to about 10 minutes; to hydrolyze the remaining 40 % of hemicellulose if water is used; d) quenching the reaction at a temperature of up about 140 °C to quench all degradation and hydrolysis reactions; and e) introducing into said reaction chamber and simultaneously removing from said reaction chamber, a volumetric flow rate of dilute acid at a temperature of up to about 140 °C to wash out the majority of the solubilized biomass components, to obtain improved hemicellulosic sugar yields.

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## AQUEOUS FRACTIONATION OF BIOMASS BASED ON NOVEL CARBOHYDRATE HYDROLYSIS KINETICS

### Technical Field:

5 The present invention is a continuation-in-part of U.S. Patent Application Serial No. 08/723,399 filed September 30, 1996, and relates to the innovation of introducing a process hot washing step at elevated temperatures (>135°C) before the hydrolysis liquors or the treated solids are flashed to atmospheric pressure in a continuous process of using hot acidic medium for hydrolysis and fractionation of biomass into its major components, in several stages.

10 10 The invention process uses a non-flowing plug flow reactor for the chemical conversions followed by using a flowing reactor at elevated temperatures solely to "hot wash" the solubilized components from the solid matrix. Alternatively, in the continuous process, a continual shrinking bed reactor may be employed.

15 The continuous process of using a hot acidic medium for fractionation of biomass components (e.g., hemicellulose and cellulose sugars, lignin, and extractives) provides high yields of sugars, e.g. xylose and glucose.

20 20 Utilization of the continual shrinking bed reactor in the fractionation of lignocellulosic biomass so that the liquid to solid ratio is kept relatively constant increases yields of the solubilized sugars and increases concentrations of the released sugars by minimizing the residence time of the liquor fraction in the reactor.

### Background Art:

25 Lignocellulosic biomass which is available in abundance can be used as an inexpensive feed stock for production of renewable fuels and chemicals. Current processes for this conversion involve chemical and/or enzymatic treatment of the biomass to hydrolyze cellulose and hemicellulose into their respective sugars. Enzymatic processes require the use of expensive biocatalysts and have the added burden of transporting lignin-slurries through the entire operating train. Current chemical processes for conversion of lignocellulosic biomass either require expensive chemical recycle or because of the prolonged exposure of the released sugars to the hydrolysis conditions, result in sugar degradation to by-products. Accordingly, current processes for producing sugars from

lignocellulosic biomass are expensive processes and low cost production of renewable fuels and chemicals using these current processes are not realized.

Further, in current continuous processes for the production of sugars from starch or lignocellulosic biomass, the reactors for hydrolysis of the lignocellulosic feedstocks by acid catalysis to produce carbohydrates for chemicals or fuels use reactor dimensions based on the bulk packing density of the feed material, thereby limiting the yields of solubilized carbohydrates as a function of hydrolysis conditions, and the reactors are expensive due to being designed for the incoming feed, and thus, under utilize the entire reactor volume.

U.S. Patent 4,880,473 entails a process for treatment of hemicellulose and cellulose in two different configurations. Hemicellulose is treated with dilute acid in a conventional process. The cellulose is separated out from the "prehydrolyzate" and then subjected to pyrolysis at high temperatures. Further, the process step between the hemicellulose and cellulose reactions require a drying step with a subsequent pyrolysis high temperature step at 400°C-600°C for conversion of the cellulose to fermentable products.

U.S. Patent 5,366,558 uses two "stages" to hydrolyze the hemicellulose sugars and the cellulosic sugars in a countercurrent process using a batch reactor, and results in poor yields of glucose and xylose using a mineral acid. Further, the process scheme is complicated and the economic potential on a large-scale to produce inexpensive sugars for fermentation is low.

U.S. Patent 5,188,673 employs concentrated acid hydrolysis which has benefits of high conversions of biomass, but suffers from low product yields due to degradation and the requirement of acid recovery and recycle. Sulfuric acid concentrations used are 30-70 weight percent at temperatures less than 100°C.

An organic solvent for pretreatment of biomass in a counter current process configuration, using a single reactor in which small particles of biomass are introduced from the top and the solvent is contacted in a counter-current fashion from the bottom of the reactor is disclosed in U.S. Patent 4,941,944. The process uses high concentrations (about 80%) of the solvent with a small amount of acid, if needed. The use of a solvent in this process necessitates recovery schemes which are cost-prohibitive insofar as the economics of the process is concerned.

Specific hydrolysis of cellulose by mild treatment with acid followed by treatment with high-pressure steam is disclosed in U.S. Patent 4,708,746; however, the use of high-pressure steam and related capital-intensive equipment does not result in complete hydrolysis.

5 Biomass hydrolysis of almost exclusively hemicellulose sugars is disclosed in U.S. Patent 4,668,340, wherein acid is introduced countercurrent to the biomass and is removed from each stage to be fed to the next in its sequence. The objective in this patent is to minimize the hydrolysis of cellulose (and the pre-hydrolysis of a lignocellulosic feed is ultimately to produce a cellulosic pulp containing 94%-97% of the feed alpha-cellulose).

0 Both U.S. Patents 5,125,977 and 5,424,417 relate to "prehydrolysis" of lignocellulosic biomass to solubilize the hemicellulosic sugars with concomitant release of some soluble lignin, thereby rendering the remaining cellulose more readily digestible with enzymes or other chemical means - thus these patents disclose only prehydrolysis.

5 Austrian Patent No.263,661 discloses dissolution of the three major components of biomass (lignin, hemicellulose and cellulose) in a flow thru reactor using hot compressed water at temperatures between 140°C-350°C. No yields of the carbohydrate fractions are disclosed in which the carbohydrates are fractionated "cleanly".

0 U.S. Patents 1,014,311; 1,023,257; 3,480,476; 4,728,367; 3,787,241; 4,706,903; 4,645,541; and 5,398,346 disclose various and sundry processes for converting starch or lignocellulosic biomass using an array of reactors; however, these patents neither acknowledge nor address any benefits associated with keeping the solid to liquid ratio the same or constant as sugars are solubilized and conveyed out of the reaction zone. Neither do these patents address the concept of using a nonflowing plug flow reactor for chemical conversions of the biomass followed by the use of a flowing reactor at elevated temperatures solely to "hot wash" the solubilized components from the solid matrix, to obtain: 1) higher yields of carbohydrate; 2) less lignin reprecipitating on the solid matrix; and 3) the production of a solid lignocellulosic substrate that is hydrolyzed by cellulases 10x the rates observed when the "hot wash" step is not used.

5 Heretofore, there has not been described a process for complete fractionation of lignocellulic biomass using a dilute acidic medium in a flow-thru process in which: 1) the solid to liquid ratio of the lignocellulosic biomass and hydrolysis liquor has been kept the same or constant as sugars and other biomass components are solubilized and conveyed out of the reaction zone; or 2) using a nonflowing plug flow reactor for chemical conversions of the biomass followed by using a flowing reactor at elevated temperatures to take advantage of novel hydrolysis kinetics of hemicellulosic sugars, wherein a process "hot washing" step is

introduced at elevated temperatures (>135°C) before the hydrolysis liquors or the treated solids are flashed to atmospheric pressure.

**Disclosure of the Invention:**

One object of the invention is to provide a process for hydrolysis and fractionation of lignocellulosic biomass into separate streams comprised of relatively pure components.

Another object of the present invention is to provide a process for hydrolysis to sugars of hemicellulose at high yields.

A further object of the invention is to provide a process for hydrolysis and fractionation of lignocellulosic biomass using dilute acid.

A still further object of the invention is to provide a process for hydrolysis and fractionation of lignocellulosic biomass using dilute acid to convert hemicellulose into monomeric sugars at high yields.

A further object yet still of the invention is to hydrolyze hemicellulose into its component sugars at high yields while providing a solid material containing much, if not almost all, of the original cellulose and some of the lignin.

Another object of the invention is to provide a continuous process for complete hydrolysis and fractionation of lignocellulosic biomass with dilute acid in a reactor configuration that minimizes the time the liquid or hydrolysis liquor spends in the reaction zone.

A further object of the invention is to provide a process for hydrolysis and fractionation of lignocellulosic biomass using dilute acid wherein higher yields of solubilized sugars are obtained in higher concentrations.

To achieve the hydrolysis and fractionation of lignocellulosic feedstocks to produce high yields of soluble sugars for fermentation to final products at high productivity, the invention utilizes a series of flow-through co-current, counter-current, or stand-alone stages which enable efficient contact of dilute acid and biomass, thereby separating solubilized components from the solid.

The fractionation may be composed of up to four functional elements linked co-currently, countercurrently, or as independent single pass units, depending upon whether the solubilized components are to be mixed or separated from other solubilized components from other functions.

In the innovative prehydrolysis mode of the invention, the hemicellulosic sugars are hydrolyzed from the biomass using aqueous conditions below pH 5.0 and reaction times and temperatures sufficient to remove the hemicellulosic sugars in a concurrent reactor mode. The hydrolyzed slurry is then cooled by either contacting with hot washing liquor or by flashing to a temperature between about 125°C-190°C, and the solids are washed with sufficient dilute acid or water, to remove 80%-100% of the solubilized biomass components. The solids and entrained liquor and the washate are then flashed to ambient pressure for further processing.

In the innovative total hydrolysis mode of the invention, the hemicellulose sugars are hydrolyzed from the biomass aqueous conditions below pH 5.0 and reaction times and temperatures sufficient to remove the hemicellulosic sugars in a concurrent reactor mode. The slurry is then conveyed to a countercurrent hydrolysis reactor to hot wash the hemicellulosic sugars away from the solid lignocellulosic substrate. The solids, either in a concurrent or countercurrent mode is then subjected to hydrolysis conditions below pH 5.0 and reaction times and temperatures sufficient to hydrolyze the cellulose. Next, the solids with entrained liquor are flashed or otherwise cooled to a temperature between about 125°C to about 200°C and washed with about two voids of an aqueous solution to remove solubilized components before recondensation occurs.

The process produces significantly higher yields of sugar in all reactor configurations compared to processes without the "hot wash" step.

#### **Brief Description of the Drawings:**

Figure 1 is a graph depicting the autohydrolysis of hardwood xylan at 183°C (◆) and 200°C (●) using flowing hot water. The dashed line is a computer simulated curve using biphasic kinetic modeling described in the literature. As is apparent a single species of xylan is released until a recalcitrant fraction, which is temperature dependent, is reached, and no more xylan can be hydrolyzed.

#### **Detailed Description of the Invention:**

The hydrolytic release of hemicellulosic sugars below pH 5.0 has been kinetically described as a pseudo first order irreversible reaction as shown below in equation (1); and gives rise to a curved kinetic release of xylan when graphed on a semilog plot as seen in Figure 1, represented as the dashed line.

## Hemicellulosic Hydrolysis:

Fraction 1 ↘

Fraction 2 → Oligomers → Monomer → Degradation Products (1)

Fraction 3 ↗

5 However, in view of data from prehydrolysis in Example I and the data from Figure 1, the invention calls into question the kinetics of equation (1) for hemicellulose hydrolysis, and this has profound implications on process designs and yields of carbohydrate.

Below is depicted the actual kinetics in accordance with the invention findings:

## Hemicellulosic hydrolysis:

0 At Reaction Temperature:

T&gt;T critical for total hydrolysis

Fraction 1<sub>total</sub> → [0<sub>1</sub>-Lignin] → Monomer degradationFraction 2<sub>total</sub> → [0<sub>2</sub>-Lignin] → Monomer degradationFraction 3<sub>total</sub> → [0<sub>3</sub>-Lignin] → Monomer degradation5 Fraction 1<sub>partial</sub> ↘ T<T critical for total hydrolysisFraction 2<sub>partial</sub> → (recalcitrant = f(T,Lignin))Fraction 3<sub>partial</sub> ↗10 T<sub>assoc</sub><140°C?[0<sub>n</sub>-Lignin] → Lignocellulosic Solid

15 The invention provides an efficient method for hydrolysis and fractionation of lignocellulosic biomass and converts it at very high yields to soluble sugars which may be fermented to the final product at high productivity, as opposed to the use of dilute acid for primarily hydrolyzing hemicellulose exclusively or for complete hydrolysis using concentrated acid.

30 The example hereinafter provided will serve to further illustrate the complete hydrolysis of lignocellulosic biomass using dilute acid in a flow-thru process.

### EXAMPLE I

A parr reactor was charged with 20g of BD yellow poplar and 100ml of water was added to wet the biomass. The reactor was sealed and submerged in a 185°C sand bath. Once the reactor reached about 160°C, the reactor was placed in a parr stand and the heater turned on to 185°C. Hot water (100ml at 205°C) was added to bring the slurry to 183°C and the reaction proceeded for about 7 minutes. At the 7 minute mark, 200ml of 220°C 0.15wt% of sulfuric acid was added while varying the temperature between about 185°C-205°C for times ranging from about 3 to about 10 minutes. The reaction was then quenched to about 140°C in a water bucket that quenched all degradation and hydrolysis reactions. Two void volumes of 140°C 0.07wt% sulfuric acid was pumped in and simultaneously pumped out (in a CSTR reactor mode) to wash out the majority (80%) of the solubilized biomass components.

The yields of the solubilized hemicellulosic sugars were from about 75% to 85%, but are obtained under less severe conditions than traditional methods not using a "hot wash". The enzymatic digestibility of the solids, using the NREL CAT 009 protocol, result in complete release of the glucose in 12 hours at 50°C, compared to 3-5 days using the traditional batch hydrolysis approach.

Figure 1 is a graph depicting xylan hydrolysis kinetics using flowing hot water.

As can be seen from this graph, the xylan hydrolysis kinetics when using a wash mode to prevent recondensation reactions from occurring, is "apparently" faster than kinetics not using a "wash" mode. Further, by including this "hot wash" process step, theoretical yields of xylose as high as 85% - 95% can be obtained using a plug flow reactor instead of the reported yields of 80% not using a "hot wash" step. Further still, the lignocellulosic substrate is more amenable to enzymatic saccharification, and one obtaining 100% conversion of the cellulose to glucose.

While the present invention uses a non-flowing plug flow reactor for the chemical conversions followed, by the use of a flowing reactor at elevated temperatures for the "hot wash" step, the invention may also use a flow-through system where fluid moves with respect to the solid lignocellulose. The lignocellulose solids may be stationary, travel in a counter-current or cross-current fashion. It is even possible for the system to use a co-current or stationary system which is agitated. One typical design is a percolation reactor. One can perform a solid-liquid separation in the flow-through system by using a screw-like device to cause the separation continuously during or at the end of prehydrolysis. Important to the

process is the movement and removal of fluid during the prehydrolysis to separate soluble products as they are released from the solid lignocellulosic residue.

Fluid need not be flowing constantly, but may be pulsed or stopped for a period of time, but it does need to move at least part of the time before the end of the prehydrolysis process. 5 Alternatively, a pulsed system may blow air or other inert gas through the system to help push out the prehydrolyzate. An air pulse may also provide an overpressure or simply agitate the system.

0 A continuous prehydrolysis reactor may also be used. Such a reactor would have lignocellulosic material driven through the reactor while fluid is passed through the material, typically in a counter-current or cross-current manner. For example, if the prehydrolysis reactor is in the configuration of a column, the lignocellulosic material may be augured into the bottom of the column and removed from the top while fluid containing the degrading compound (s) is added at the top and passes through the biomass to be removed at the bottom. The reverse configuration is also possible. Alternatively, the lignocellulosic substrate may be driven laterally while fluid is applied on top and allowed to percolate down to be removed at the 15 bottom.

15 Appropriate particle sizes vary with the feedstock and its inherent physical properties. Particle sizes appropriate for ground wood are in the range of about 0.1 mm to 30mm, preferably in the range of 0.5mm to 4mm. Other materials may be larger or smaller depending 20 on the particular materials, particularly those having at least one thin dimension such as paper or straw. If one relies on the effects of gravity or floatation to cause movement of the solid lignocellulosic material with respect to the fluid, then particle size may need to be adjusted appropriately to permit solid/liquid movement in the time period of the prehydrolysis. Optimum sizes will depend on the particular lignocellulosic material used and the reactor size 25 and construction and are readily determinable by routine experimentation.

The lignocellulosic substrate may consist of hardwood, grasses, softwood, waste paper and pulp, municipal wastes, agricultural wastes such as straws, corn cobs, corn stover, biomass of all types, etc. and mixtures thereof. The choice of lignocellulosic substrate will depend on the availability and cost of lignocellulosic materials.

30 In the present invention, the reactor generally may have solids content of between about 5% and 50%, preferably about 8%-30%, when the solids are present with the liquid at the end of the prehydrolysis. The higher solids content are generally more desirable but the

concentration is limited by the designs of the reactor and the need for fluid to flow throughout the solids. At the beginning of the prehydrolysis, the solids content may range from 0 to 100% by weight as the reactor may initially contain only the lignocellulosic solids or the degrading fluid.

5 While the invention has been described with respect to specific embodiments, it is to be expected that, by the application of current knowledge, those skilled in the art may readily modify or adapt for various applications such specific embodiments without departing from the generic concept, and such adaptations and modifications should and are intended to be comprehended within the meaning of the range of equivalence of the disclosed embodiments.  
0 Further, it is to be understood that the terminology employed herein is for purposes of description and not limitation.

Claims

1. A multi-function process for hydrolysis and fractionation of lignocellulosic biomass to separate hemicellulosic sugars from other biomass components comprising extractives and proteins; a portion of a solubilized lignin; cellulose; glucose derived from cellulose; and insoluble lignin from said biomass, the improvement comprising:
  - a) introducing either solid fresh biomass or partially fractioned lignocellulosic biomass material containing entrained water or acid at pH < 5.0 into a reactor and heating to a temperature of up to about 185°C to about 205°C;
  - b) allowing the reaction to proceed to a point where about 60% of the hemicellulose has been hydrolyzed, in the case of water only for about 6-10, or in the case when acid is present for about 5-10 minutes for complete dissolution;
  - c) adding a dilute acid liquid at a pH below about 5.0 at a temperature of up to about 205°C for a period ranging from about 5 to about 10 minutes when water is used in step b);
  - d) quenching the reaction at an average temperature of up to about 140°C to quench all degradation and hydrolysis reactions;
  - e) introducing into said reaction chamber and simultaneously removing from said reaction chamber, a volumetric flow rate of dilute acid at an average temperature of up to about 140°C to wash out the majority of the solubilized biomass components, to obtain improved hemicellosic sugar yields and prevent recondensation reactions from occurring.
2. The process of claim 1, wherein, in step (e) said dilute acid is introduced in an amount about 2 times the volume of the reaction chamber.
3. The process of claim 1 wherein said dilute acid is a mineral acid.
4. The process of claim 3, wherein said mineral acid is selected from the group consisting of sulfuric acid, phosphoric acid, nitric acid or carbonic acid.
5. The process of claim 4, wherein said dilute acid is sulfuric acid.
6. The process of claim 5, wherein in step (e), 0.15 weight percent of sulfuric acid is used, and in step e, 0.07 weight percent of sulfuric acid is used.
7. The process of claim 6 in which the reactor is a plug flow reactor.
8. The process of claim 7 in which the reactor is a continual shrinking bed reactor.

9. The process of claim 8, in which the continual shrinking bed reactor is a cylindrical reactor with "broken" internal flights to allow the biomass to fall back to maintain a relatively constant solid to liquid ratio.

10. The process of claim 9 wherein the volumetric flow rate is sufficient to keep the solid and liquid at a constant ratio throughout said process so as to increase the linear velocity.

5 11. The process of claim 6 wherein, in step (e), said majority of the solubilized biomass components is 80%-100%.

12. The process of claim 11, wherein said biomass is yellow poplar.

13. The process of claim 12, wherein said biomass is corn stover, rice-straw, a soft wood mix, 0 bagasse, or clarified municipal solid waste.

## AMENDED CLAIMS

[received by the International Bureau on 14 August 2000 (14.08.00);  
original claims 1 to 13 replaced by amended claims 1 to 13 (2 pages)]

1. In a multi-function process for hydrolysis and fractionation of lignocellulosic biomass to separate hemicellulosic sugars from other biomass components comprising extractives and proteins; a portion of a solubilized lignin; cellulose; glucose derived from cellulose; and insoluble lignin from said biomass, the improvement comprising:
  - a) introducing either solid fresh biomass or partially fractionated lignocellulosic biomass material containing entrained water or acid at pH < 5.0 into a reactor and heating to a temperature from about 185°C to about 205°C;
  - b) allowing the reaction to proceed to a point where about 60% of the hemicellulose has been hydrolyzed, in the case of water only for about 6-10 minutes, or in the case when acid is present for about 5-10 minutes for complete dissolution;
  - c) adding a dilute acid liquid at a pH below about 5.0 at a temperature of up to about 205°C for a period ranging from about 5 to about 10 minutes when water is used in step b);
  - d) quenching the reaction at an average temperature of up to about 140°C to quench all degradation and hydrolysis reactions;
  - e) introducing into said reaction chamber and simultaneously removing from said reaction chamber, a volumetric flow rate of dilute acid at an average temperature of up to about 140°C to wash out the majority of the solubilized biomass components, to obtain improved hemicellulosic sugar yields and prevent recondensation reactions from occurring.
2. The process of claim 1, wherein, in step (e) said dilute acid is introduced in an amount about 2 times the volume of the reaction chamber.
3. The process of claim 1 wherein said dilute acid is a mineral acid or carbonic acid.
4. The process of claim 3, wherein said mineral acid is

selected from the group consisting of sulfuric acid, phosphoric acid, and nitric acid.

5. The process of claim 4, wherein said dilute acid is sulfuric acid.

6. The process of claim 5, wherein in step (c), 0.15 weight percent of sulfuric acid  
5 is used, and in step (e), 0.07 weight percent of sulfuric acid is used.

7. The process of claim 6 in which the reactor is a plug flow reactor.

8. The process of claim 7 in which the reactor is a continual shrinking bed reactor.

9. The process of claim 8, in which said continual shrinking bed reactor comprises  
means to allow the biomass to fall back to maintain a constant solid to liquid ratio.

10. The process of claim 9 wherein the volumetric flow rate is sufficient to keep the  
solid and liquid at a constant ratio throughout said process so as to increase the liner velocity.

11. The process of claim 6 wherein, in step (e), said majority of the solubilized  
biomass components is 80 to 100 weight percent.

12. The process of claim 11, wherein said biomass is yellow poplar.

15. The process of claim 12, wherein said biomass is corn stover, rice-straw, a soft  
wood mix, bagasse, or clarified municipal solid waste.

**STATEMENT UNDER ARTICLE 19**

Before contending with the allegation that claims 1-13 lack an inventive step in view of US Patent 4,615,742, when this patent is combined with one or more other such documents, such that the combination would be obvious to a person skilled in the art, it is believed useful to summarize the essentials of the improved multi-function process for hydrolysis and fractionation of lignocellulosic biomass of the invention to establish clearer distinction between the invention process and the process disclosed in U.S. Patent 4,615,742.

In the multi-function process art for hydrolysis and fractionation of lignocellulosic biomass to separate hemicellulosic sugars from other biomass components, applicant has invented an improvement whereby complete fractionation of lignocellulosic biomass is accomplished by use of introducing a "hot washing" step at elevated temperatures greater than about 135°C before the hydrolysis liquors or the treated solids are flashed to atmospheric pressure to obtain: higher yields of carbohydrate; less lignin reprecipitating on the solid matrix; and production of a solid lignocellulosic substrate that is hydrolyzed by cellulases at 10x the rates observed when the "hot wash" step is not used.

Review of US Patent 4,615,742 reveals that its hydrolysis and fractionation process is completely devoid of a "hot wash" step such as that of the present invention process. The "hot wash" step of the present invention affects washing out of the majority of the solubilized components from the solid matrix to obtain improved hemicellulosic sugar yields and prevent recondensation reactions from occurring.

This "hot wash" step of step e) of applicant's claims is neither hinted at, suggested or taught in US Patent 4,615,742.

U.S. Patent 4,615,742 only disclose a progressive batch process of hydrolysis for producing sugar from lignocellulosic feedstock by passing a stream of dilute acid serially through a plurality of percolation hydrolysis reactors.

Further, U.S. Patent 4,615,742 fails to disclose the claimed pH condition of >5.0. However, applicant would also point out that U.S. Patent 4,615,742 also lacks applicant's "hot wash" as recited in step e).

Accordingly, the absence of these aforementioned process requirements are fatal to the use of U.S. Patent 4,615,742 as an obviousness rejection reference alone. Further, contrary to the requirement in the Search Report, this patent has not in fact been cited in combination with other documents. Therefore, the rejection is misplaced under category Y. Apparently, category X for a single document citation under the lack of novelty standard may have been intended.

As is clearly noted on page 4, lines 19-22 of applicant's specification, by virtue of use of a "hot wash" higher yields of carbohydrate are obtained; less lignin is reprecipitated on the solid matrix; and the production of solid lignocellulosic substrate that is hydrolyzed by cellulases is at 10x the rates observed when the "hot wash" step is not used.

Further, as noted on page 9 of applicant's specification at lines 8-20, use of the "hot wash" results in complete release of the glucose in 12 hours at 50°C, compared to 3-5 days using the traditional batch hydrolysis process.

Further still, as can be seen from FIG. 1, which is a graph depicting xylan hydrolysis kinetics using flowing hot water, the xylan hydrolysis kinetics when using the invention "hot wash" mode prevents recondensation reactions from occurring faster than kinetics not using the invention "hot wash" mode.

In view of the fact that U.S. Patent 4,615,742 fails to hint, disclose, or teach the requisite pH and "hot wash" conditions required by the invention process, it is clear that this patent fails to render the claims as presently amended obvious.

As revised, the claims on replacement pages 12-13 now define the invention with greater accuracy.

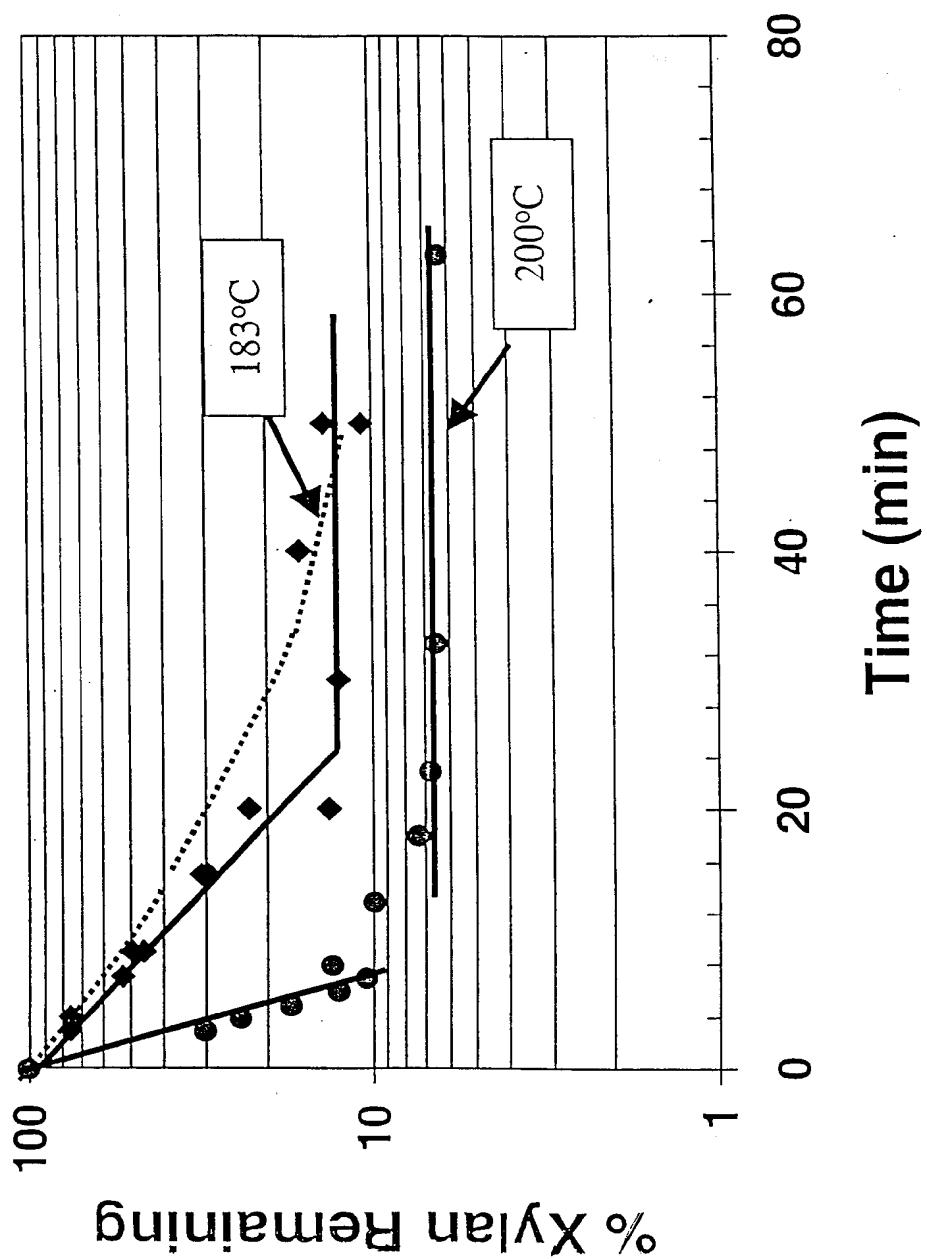


Figure 1

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/08971

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :Please See Extra Sheet.  
US CL : 127/1, 37; 435/105; 536/56, 124, 127  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 127/1, 37; 435/105; 536/56, 124, 127

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

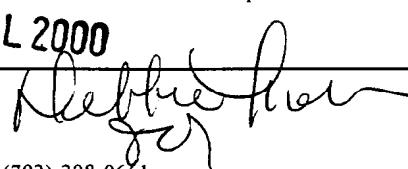
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,615,742 A (WRIGHT) 07 October 1986, col. 1, line 14 to col. 10, line 18.	1-13

Further documents are listed in the continuation of Box C.  See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 28 JUNE 2000	Date of mailing of the international search report 13 JUL 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARK BELL Telephone No. (703) 308-0661 

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/08971

A. CLASSIFICATION OF SUBJECT MATTER:  
IPC (7):

B01J 3/00; C13K 1/02; C12P 19/02; C07G 17/00; C07H 1/00, 3/00, 1/06, 1/08